UPWARDS MIGRATION OF IRON AND PHOSPHORUS COMPOUNDS IN ANOXIC SEDIMENTS FROM A MESOTROPHIC LAKE ON THE PRECAMBRIAN SHIELD

DECEMBER 1991

Ontario
Environment
Environnement

ISBN 0-7729-9061-1

UPWARDS MIGRATION OF IRON AND PHOSPHORUS COMPOUNDS IN ANOXIC SEDIMENTS FROM A MESOTROPHIC LAKE ON THE PRECAMBRIAN SHIELD

Report prepared for:

Water Resources Branch
Ontario Ministry of the Environment

Report prepared by:

G.K. Nurnberg, Faculty of Science, York University
and
P.G. Manning, National Water Research Institute

December 1991

Cette publication technique
n'est disponible qu'en anglais.

Copyright: Queen's Printer for Ontario, 1991
This publication may be reproduced for non-commercial purposes
with appropriate attribution.

PIBS 1756
log 91-2345-084

DISCLAIMER

This report was prepared for the Ontario Ministry of the Environment as part of a ministry-funded project. The views and ideas expressed in this report are those of the author and do not necessarily reflect the views and policies of the Ministry of the Environment, nor does mention of trade names or commercial products constitute endorsements or recommendation for use.

92-03419/

ABSTRACT

Simultaneous upwards migration of phosphorus (P) and iron (Fe) was observed in anoxic sediment from a mesotrophic bay of a Precambrian Shield lake. Highly reproducible samples of the anoxic hypolimnetic water and sediment were obtained by subcoring large cores in the laboratory. Changes in total P (TP) and total Fe (TFe) and their fractions, determined by chemical extractions and Mössbauer spectrometry, and in total manganese (Mn) were recorded in both sediment and overlying water of these closed systems after 26 days of incubation. Concentrations of TP, TFe, reductant soluble P (NAIP and BD extractable P) and some iron fractions decreased significantly in the sediment while TP, soluble reactive P, total reactive P and TFe increased in the overlying water. Water gains and sediment losses were significantly correlated indicating upwards migration of the P and Fe compounds. The molar Fe-to-P ratios of the decreases in the sediment and the increases in the water were similar, indicating the same origin of Fe and P compounds. The release of P and Fe was redox related: cores with a sediment depth of 5 cm or less became aerated and had redox potentials above 160 mV and lower release. Simultaneous upward migration of Fe and P, but not Mn, and the redox-dependent release are consistent with Mortimer's classic theory on the release of phosphorus after the reduction of hydrated iron oxides.

INTRODUCTION

Phosphorus (P) concentrations in lake sediments are typically three orders of magnitude higher than in the lake water. Some of this sediment P, e.g., apatite, can be called "refractory" and is believed to remain un-involved in the biotic P cycle of the lake. Another fraction of sediment P is soluble as orthophosphate in the sediment pore water or can easily be dissolved when the sediment becomes reduced. This type of sediment P can be released into the overlying water under anoxic conditions and may then fertilize the lake water. The quantity of this biologically active P in the sediment may be correlated to certain iron fractions, since iron hydroxides from oxygenated environments sequester ortho-phosphate, but dissolve and are released simultaneously with P when reduced, if not precipitated as iron sulphides (Mortimer 1941; Einsele 1938).

For the management of lakes with anoxic P release, it is important to know the pool size of potentially releasable sediment P and the depth involved in this process. Evidence that P migrates upwards in sediments overlain by anoxic water has been reported before (Carignan and Flett 1981) and the present study supports this theory as well. We investigated several sediment fractions of P and iron simultaneously during anoxic incubation. Furthermore, concentration changes of the overlying water are recorded and compared to the changes in the sediment.

Sediment from a bay that has turned mesotrophic within the last 100 years of a 90 km^2 oligotrophic lake on the Precambrian Shield, Gravenhurst Bay of Lake Muskoka, was selected for the studies. Hardwater lakes serving as recreation and water resource, located not far from metropolitan areas, are quite commonly eutrophic, but even soft water lakes in the vicinities of cities may become eutrophied in the future (Lake Muskoka is 200 km north of Toronto, Ontario). In Gravenhurst Bay, hypolimnetic P and Fe concentrations increase during periods of anoxic stratification (Nürnberg 1987).

Large sediment cores were subsampled in the laboratory to generate replicates with different sediment depths. In this way, the effect of sediment depth on release could be tested and mass changes of several fractions of iron (Fe) and P in the sediment could be related to changes in the overlying anoxic water after incubation. The shape of sediment Fe and P profiles, concentration changes and molar Fe-to-P ratios were used to test for upwards migration.

Manganese (Mn) was also included in the analysis. It is not involved in the release of P according to the classical model (Mortimer 1941), but is released at higher oxygen concentrations. It was used to distinguish if the observed correlated release of Fe and P is likely due to the dissolution of hydrated iron oxides after reduction or simply due to sediment disturbances.

MATERIALS AND METHODS

Study Site

Gravenhurst Bay (44°56′ 79°23′, mean depth: 9.8 m, surface area: 179 ha) is a recently eutrophied bay (within the last 100 yrs) of dimictic Lake Muskoka. Water samples typically show oxygen depletion in the hypolimnion and increased P, Fe and Mn concentrations (Fig. 1a, b). Sulphate concentration is decreased and hydrogen sulphide slightly increased in the hypolimnion (Fig. 1c). The anoxic factor is 43 days on average (Nürnberg 1988); this factor indicates the number of days on which an area of the sediment equal to the whole lake surface is overlain by anoxic water. Internal P load, as determined from maximum, increases in hypolimnetic P mass averages 140 mg m^{-2} lake surface area $summer^{-1}$ (Nürnberg 1988). Gravenhurst Bay is poorly buffered but not acid (Fig. 1c) with an average alkalinity of 10 mg l^{-1} and is relatively clear (dissolved organic carbon, 3.6 mg l^{-1}).

Sampling and Incubation

Two medium sized cores (6 cm i.d.) and 6 large cores (9 cm i.d.) were taken with a Kajak Brinkhurst corer from a boat at 16 m depth in September 1986. At this time the sediment had been overlain by anoxic water for approximately one month; EH, 36 mvolt; total P (TP), 0.22 mg l^{-1}; soluble reactive P (SRP), 0.21 mg l^{-1}; total Fe (TFe) consisted entirely of free ferrous iron (Fe^{2+}), 7.6 mg l^{-1} (Fig. 1). 1 cm sediment sections of the medium sized cores were analyzed to obtain chemical profiles.

The large cores were re-cored by hand in the laboratory (succeeding day) with small tubes (2.5 cm i.d., 35 cm height). In this way, high reproducibility was insured for small cores of the same large core; this technique may, however, introduce artifacts due to increased compaction and handling. From each large core, three small cores were taken simultaneously to yield approximately 5, 10 or 15 cm of sediment and 20 to 30 cm of hypolimnetic water. (Three small cores were lost in this step.) On the following day, water and sediment of three small cores from three different large cores were analyzed. The average of these cores was taken as initial concentrations for some mass balance calculations. Mass changes of the sediment were also calculated from the concentration in small cores after incubation in comparison to the initial small core from the same large core ("matched cores") to see if sediment heterogeneity affects mass balances.

Twelve small cores (2 from each of the large cores) were then incubated for 26 or 27 days at 9-11°C in the dark. To prevent any leakage of oxygen into the cores through the plastic walls or the stoppers at either end, the cores were immersed in a water bath filled with ascorbic acid solution as reducing agent. Hypolimnetic conditions were simulated by keeping the water dark, still, unstirred and without any addition of nitrogen gas.

At the end of the anoxic incubation period, the cores were carefully opened and an aliquot was withdrawn immediately for a Fe^{2+} analysis based on batho-phenanthrolein (Nürnberg 1984). Next, EH, pH and temperature (for the correction of EH, Nürnberg et al. 1986) of

the water were determined simultaneously. Water for the analysis of P and metal fractions was withdrawn with a tubing on a syringe down to ca 10 cm above the sediment to avoid sediment disturbance and air contact. In earlier experiments, layering of the water column 5 cm and higher above the sediment was undetectable. SRP and TRP (total reactive P) were analyzed immediately to minimize air exposure and possible formation of hydrous Fe oxides (Nürnberg 1984). The water for the determination of total P, Fe and Mn was placed into vials to be analyzed later with potassium persulfate digestion (Menzel and Corwin 1965). The sediment of the core was sectioned in 5 cm intervals by pushing the sediment upwards with a plunger. The sediment was stored in tightly-closed plastic vials at 4°C (-10 °C for Mössbauer analysis) and rigorously mixed before aliquots were withdrawn for triplicate analysis (within 8 wks; 52 wks for Mössbauer analysis).

The water directly overlying the sediment (0-10 cm) was syphoned off and discarded. Therefore, no mass balances can be computed for the cores, but changes in the sediment can be compared to changes in the water of 10 to 25 cm above the sediment.

Sediment Analysis

Water content and organic content, as LOI (loss on ignition), were determined by drying and igniting aliquots of the samples at 95°C (24 h) and 500°C (1-2 h), respectively, to constant weight.

Reduced sediment iron (Fe_{red}) in silts, clays and chlorites, oxidized iron (Fe_{ox}), as hydrated iron oxides in clays and humic or fulvic acid complexes, pyrite (FeS_2) and vivianite were determined by Mössbauer diffraction analysis. Mössbauer spectra were recorded at room-temperature on a 512-channel spectrometer and resolved using computer programs of Stone (1967). The areas and half-widths of peaks within a quadrupole doublet were constrained to be equal; Lorentzian line-shapes were assumed. "Goodness of fit" of the computed and recorded spectra was determined with statistical (Chi-squared values) and visual criteria. The spectrometer was calibrated against iron foil.

Optical microscopy revealed the presence of some opaque spherical framboids characteristic of FeS_2; weak pyrite lines were observed in X-ray diffraction patterns. Spectral resolution was therefore based on three doublets, $Fe_{red,}$ Fe_{ox} and FeS_2 (Fig. 2). The positions and half-widths of the pyrite peaks were constrained at values corresponding to isomer shift (IS)= 0.31 mm s^{-1}, quadrupole splitting (QS)= 0.61 mm s^{-1} and half-width (HW)= 0.30 mm s^{-1} (Manning et al. 1979). Most spectra were fitted satisfactorily with values of chi-squared between 500 and 750 (Fig. 2). However, in spectra of the small cores from two large cores, a shoulder on the Fe_{red} spectral peak was seen at 2.3 mm s^{-1}. Computation placed this fourth doublet consistently at energies similar to those of vivianite (Nembrini et al. 1983) with an intensity of 8 and 19% of total iron. These samples also contained comparably higher concentrations of TP, TFe and the P fractions. The presence of vivianite in these few samples was confirmed by x-ray diffraction methods and is supported by equilibrium calculations based on pH, ferrous iron and SRP concentrations in the water overlying the sediment.

TP, TFe and Mn were determined using dried sediment after ignition and boiling in 8% hydrochloric acid solution according to Andersen (1976). This method had been developed and tested for TP sediment content. The extraction of TFe with HCl appears to be incomplete since sediment analyzed by bomb digestion (Agemian and Chau, 1975), reveals a TFe concentration of ca 120% of the one reported here. Correlations of the HCl extracted TFe concentrations with Fe_{ox} concentration suggest that the HCl based analysis does not completely analyze the Fe_{red} fraction bound in silts and clays. The TFe concentrations of the large core profiles were analyzed by bomb digestion. The Fe concentrations of the "mini cores" were analyzed with the HCl method.

BD-P was determined with the (0.11 M) bicarbonate dithionite extraction modified from Psenner et al. (1984), (Nürnberg 1988). This extraction is more specific to Fe-P associations, which are readily released under anoxic conditions, than the more widely used citrate dithionite bicarbonate extraction (CDB, e.g., Williams et al. 1971). It does not include a complexing agent responsible for the dissolution of Al-P complexes. NaOH-P in

the residue after the BD extraction, dissolved in 1 N NaOH for 24 hrs, was measured to investigate the effects of P complexed with Al and metals in organic acids (Psenner et al. 1984; Nürnberg 1988). NaOH-Fe was determined in the same extraction as a measurement of Fe combined with organic (humic and fulvic) acids. Apatite and NAIP (non apatite inorganic P) were analyzed according to Williams et al. (1976).

All phosphate analyses were done with the molybdenum blue method (Stainton et al. 1977). The Fe and Mn analysis after extraction and digestion and TFe and Mn of the water were determined by atomic absorption spectroscopy.

Precision of all analyses (3-5 SE in % of mean), accuracy (97-109%) and recovery (93-113%) of the P extractions were determined on a routine basis and are similar to those reported earlier (Nürnberg 1988). Trailing of BD-P extraction, determined by a second extraction, was circa 10% in these P rich sediments, and is comparable to the 98-110% recovery for lake sediments from seven different lakes (Nürnberg, 1988).

RESULTS AND DISCUSSION

Sediment Profiles

The analysis of 1 cm sections of two medium sized cores (6 cm i.d.) from the anoxic hypolimnion reveals elevated surface concentrations (0-4 cm) of TP, BD-P (the fraction which is readily released under anoxic conditions), (Nürnberg 1988), NaOH-P and NaOH-Fe (the fractions bound to aluminum and organic acids), TFe and Fe_{ox} (Fig. 3). Water content decreases gradually from 96% at the surface to 88 % at a depth of 12 cm. LOI drops from 30% within the 0 to 3 cm layer to 23% between 4 and 12 cm. The "refractory" portion i.e., P in apatite (110 ± 15 ug g drywt^{-1}) and Mn (Fig. 3a) are more evenly distributed. 70-80% of total Fe was in the form of Fe_{ox} (Fig. 3b) with the Mössbauer parameters of isomer shift IS = 0.37 mm s^{-1}, quadrupole splitting QS = 0.75 mm s^{-1} and half-width HW = 0.56 mm s^{-1} (Fig. 2). Most of this fraction likely presents amorphous iron oxides and iron oxide crystals of less than 200 Å diameter, since no crystalline ferric compounds could be resolved by x-ray

diffractometry. A large fraction of Fe_{ox} has been found consistently in deep sediments of Canadian lakes (Manning & Jones 1982) and likely belongs to a larger complex of humic/ fulvic material, clay and phosphorus residues, that dissolve at a lower redox potential than free iron oxides. Fe_{red} (Mössbauer parameters IS= 1.12 mm s^{-1}, QS=2.61 mm s^{-1}, HW= 0.56 mm s^{-1}, Fig. 2) accounts for 25% of TFe on average and pyrite for 5%; both fractions are rather evenly distributed throughout the upper 12 cm of the sediment (Fig. 3b).

The molar TFe-to-TP ratio is much larger than 2 (5.8 - 7.5, Fig. 3c), which is the minimum for P adsorption to take place (Tessenov 1974). The high ratio indicates that the sediments have a high adsorption capacity for P under oxic conditions. The molar ratios of the NaOH fractions (P and Fe bound to organic acids or aluminum) are much lower (1.4 - 3.1, Fig. 3c).

The occurrence of P and Fe maxima at the sediment/water interface, without a distinct peak in the sediment below, is typical for sediments releasing P and Fe while overlain by anoxic water and suggests upwards migration (Carignan and Flett 1981).

Upward Migration of P and Fe

Upwards migration is also supported by a more detailed investigation of Fe and P fractions in the sediment and water during incubation. Average P concentrations in the small cores were TP, 3.9 mg g dry $weight^{-1}$; BD-P, 2 mg g dry $weight^{-1}$ and Fe, 40 mg g dry $weight^{-1}$ before incubation. These concentrations are higher than those of the larger cores and water content is often lower; the discrepancies might be due to sediment heterogeneity at different sampling locations. Sediment TP, BD-P, NAIP, TFe, Fe_{ox} and Fe_{red} decreased substantially and significantly during incubation in the upper sediment layer (Table 1) and were significantly correlated among each other. The same trend exists for the lower sediment layer; however, there are significant changes only for NAIP and the iron fractions (Table 1). The proportion of BD-P, NAIP, Fe_{red}, Fe_{ox} and vivianite remained constant; the lack of significant changes of the P and Fe proportions likely reflects the fast achievement of equilibrium conditions during incubation. The loss of similar proportions of Fe_{red} and Fe_{ox}

during incubation could indicate the presence of mixed-valence Fe^{3+}-Fe^{2+} hydrous oxides in these sediments. The other measured fractions and Mn did not experience any significant change ($p > 0.05$); LOI and water content increased slightly (Table 1). The absolute loss of TP was usually ca. twice that of the BD-P loss. Unless a (not determined) fraction other than BD-P is released as well, this loss might indicate that BD-P is replaced from a non-BD fraction during anoxic incubation. This idea is also supported by the observed correlation of the Fe and P fractions.

TP, as well as TFe losses were similar for different depths (0-5, 5-10 cm). Losses from the 0-5 cm sediment layers were not larger in cores without the deeper layers, indicating that P and Fe from the deeper sediment layer migrate upwards and are released into the water.

After incubation, the increases in the overlying water (before incubation n=3, mg l^{-1}) of TP (0.13), SRP (0.03), TRP (0.06), TFe (1.08), Fe^{2+} (0.98) and Mn (0.17) were variable (Table 2), but were significantly correlated among each other except for Mn. pH (6.4) did not change significantly and EH, artificially elevated by coring (257 mvolt), decreased. The release rates of TP and the P fractions (Table 2) are comparable to those found in larger cores (6 cm i.d.) collected in the previous year at a similar location (average of 6 cores: TP, 5.27; SRP, 5.89; TRP, 5.08 mg m^{-2} d^{-1}; Nürnberg 1988).

All increases, except those of Mn and BD-P, were significantly correlated with corresponding total losses in the sediments of matched cores (i.e., sediment mass changes are calculated from the same large cores) (Table 3, Fig.4). The water increases were not correlated to losses in the sediment calculated from the average concentration of all the initial sediment cores. This result indicates that sediment heterogeneity can defeat the attempt of finding evidence for the matched changes of P and Fe in sediment and water unless cores stem from the same (this study) or closely located (Nürnberg 1988) sampling spots.

To account for all the decreases in sediment TP, the water immediately overlying the sediment must have had a concentration of 30 - 100 mg l^{-1} P as compared to the average

0.64 mg l^{-1} in the upper water layer. Since concentrations as high as that are unknown in the open hypolimnia of lakes and would lead to an unrealistically high P release rate (Nürnberg 1987), the P and Fe mass at the sediment water interface likely becomes re-adsorbed rapidly, if oxygenated. The observed correlated changes of P and Fe and their fractions in sediment and water, and the lack of significant correlations for Mn, NaOH-P and NaOH-Fe, indicate that P likely is released from hydrated iron oxides in these sediments. Redox dependent correlated release of P and Fe and a conspicuous uncorrelated release of Mn were also observed in the more calcareous sediments of Lake of Constance (Frevert 1979).

Correlated mass changes in sediment and water were also observed earlier in the P release of seven different lakes (Nürnberg 1988). Furthermore, evidence of correlated upwards migration of P and Fe compounds was found from incubation studies of sediments from two eutrophic dams (Helbig et al. 1981). Longterm (more than a year) incubation revealed oxygen dependency, correlated release of P and Fe, decrease of P (19%) and Fe (12%) in the sediment after incubation and ratios of released Fe-to-P in the water similar to those of the inorganic fraction in the sediments before incubation.

Fe-to-P Ratio in Water and Sediment

If P and Fe increases in the anoxic water originate in P and Fe compounds of the underlying sediment, ratios of Fe to P should be similar in the sediment decreases and the water gain, as long as no secondary diagenesis is taking place, especially precipitation of iron sulfides. Precipitation of iron sulfide is not to be expected, since free sulfides (from H_2S) were 0.05 mg l^{-1} in the anoxic lake water, and remained below 1 mg l^{-1} during incubation. Also, only less than 5% of the sedimentary iron is bound in pyrite (Table 1, Fig. 3b).

The molar Fe-to-P ratios are similar (8) for both sediment loss (0-5 cm) and water gain in matched cores, supporting the hypothesis of the same origin of the released P and Fe compounds. After incubation, the ratios are slightly lower in the sediment and usually

higher (though similar as average) in the water (Table 4). The Fe-to-P ratios in the initial sediment and water are usually lower than the ratio of the concentration changes. Although the differences of these ratios are not significant (analysis of variance of all ratios, $n=62$, $p=0.223$), the trend is consistent and may indicate that the amount and proportion of releasable Fe is higher than that of releasable P.

The BD fractions of P (Nürnberg 1988) and Fe can be used as an approximation of these releasable fractions. BD-Fe (separated like BD-P, with subsequent atomic absorption spectroscopy) was not determined in this study, but in cores taken the preceding year also in Gravenhurst Bay, the proportion of Fe in BD extractable form was indeed significantly higher than that of BD-P ($x \pm SE$, 0.27 ± 0.012 versus 0.167 ± 0.004, $n=10$). Furthermore, the molar Fe-to-P ratio of the BD fractions in the sediment of those cores before incubation was similar to the ratio in the water gain, while the ratio of total sediment Fe and P before incubation was smaller.

Sediment Depth and EH

The dependence of P and Fe release on the depth of the sediment in each core could serve as an additional indication for the migration of P and Fe compounds if it exists. The theory here would be that the more sediment is in the core, the more compounds are available for upward migration and release. Indeed there exists a pattern of decreased release of TP, SRP, TRP, TFe and Fe^{2+} at the shallow depth of 5 cm (e.g. Fig. 5). In these cores , however, EH is conspicuously high (244, 176 and 204 mV), which indicates that hydrous iron oxides still prevail and adsorb phosphate (above the theoretical EH of 160 mV at $pH=6$, based on equilibrium conditions, Stumm and Morgan 1981) and consequently have lower release (Table 2).

Moreover, stepwise multiple regression analysis of water changes versus depth, EH of the water after incubation, sediment concentrations and changes in BD-P, TP and TFe after incubation selects EH as the only independent variable (alpha level to enter a variable, 0.15;

e.g., TP changes= 257-1.03 EH, r^2= 0.574, n=12. Fig. 6). This result indicates that the sediment oxygen demand is dependent on the depth of the sediment. Therefore, care has to be taken in core tube studies to provide enough sediment that the redox potential is not artificially increased and release rates decreased. Depth dependency of release might be valid for a longer time span or shorter sediment cores, but it cannot be separated from the effect of EH in this study. It becomes clear, however, that sediment layers as deep as 10 cm are responsible for P and Fe release in Gravenhurst Bay's sediment. The observed correlation of release with redox potential indicates the involvement of iron hydroxides in the release of P in these sediments and is consistent with Mortimer's (1941) classical theory.

Incubation experiments likely reflect in situ events during anoxic summer stratification. The slight changes of the Fe-to-P ratios during incubation indicate that proportionally more Fe than P is released from profundal sediments of lakes with long anoxic stratification periods. This event may eventually impoverish the sediments in Fe; Fe mixing into surface water during thermocline erosion may lead to Fe loss from the lake (Nürnberg unpublished data). Although not found during the study period, redox potentials in these lakes can become low enough for the formation of FeS, which further contributes to the decrease of "available" Fe (Carignan and Tessier 1988). Such a decrease of Fe-to-P sediment ratios means a decrease in Fe absorption capacity (Cornwell 1987).

It appears that a large proportion of the sediment P (up to 26%) migrates upwards to the sediment-water interface during anoxic stratification. Most of this sediment loss is probably re-adsorbed with the onset of oxic conditions, since release rates based on the much lower increases in the upper water are realistic (Nürnberg 1987). If further studies confirm these events, in-lake restoration could be made more efficient if the timing is considered: the sediment-water interface could be syphoned off during anoxia to effectively decrease P concentrations. This technique would be a less costly and very efficient alternative to sediment dredging. Since P release rates are positively correlated to sediment P concentration (Nürnberg 1988), this technique would lead to lower internal P loads and lower whole lake P concentrations, thus, ultimately decreasing the trophic state of the lake.

Simultaneous upwards migration of phosphorus and iron as demonstrated for the Gravenhurst Bay sediments supports the classical theory that high concentrations of P in anoxic hypolimnia form after the dissolution of P and hydrated iron oxide complexes (Mortimer 1941; Einsele 1938). But more recent studies in eutrophic systems suggest that P is also released from bacteria at the sediment surface (Fleischer 1986; Gächter et al. 1988) and that iron-controlled P release is of less importance (review by Boström et al. 1988). The importance of bacteria in anoxic P release of softwater lakes on the Precambrian Shield is probably small as compared to hypertrophic systems, where bacterial abundance is high and P to Fe ratios in sediments and hypolimnetic water cannot be explained by the classical theory alone (Gächter et al. 1988).

ACKNOWLEDGEMENTS

We gratefully acknowledge Pat Rassmussen's able help in the field and the laboratory, and appreciate the support from staff of the Ontario Ministry of the Environment in Dorset. The comments by Peter Dillon, Bruce LaZerte, Edward Tipping and two anonymous reviewers are greatly appreciated. Part of this research was funded by a McLean Foundation grant to Don McQueen, York University. The principal author was supported by a postdoctoral fellowship from the Natural Sciences and Engineering Research Council of Canada.

REFERENCES

Agemian, H. and A.S.Y. Chau. 1975. An atomic absorption method for the determination of twenty elements in lake sediments after acid digestion. Analyt. Chim. Acta 80: 61-66.

Andersen, J.M. 1976. An ignition method for determination of total phosphorus in lake sediments. Wat. Res. 10: 329-331.

Boström, B., J.M. Andersen, S. Fleischer and M. Jansson. 1988. Exchange of phosphorus across the sediment-water interface. Hydrobiol. 170: 229-244.

Carignan, R. and R.J. Flett. 1981. Postdepositional mobility of phosphorus in lake sediments. Limnol. Oceanogr. 26: 361-366.

Carignan, R. and A. Tessier. 1988. The co-diagenesis of sulfur and iron in acid lake sediments of southwestern Quebec. Geochim. Cosmochim. Acta 52: 1179-1188.

Cornwell, J.C. 1987. Phosphorus cycling in arctic lake sediment: adsorption and authigenic minerals. Arch. Hydrobiol. 109: 161-179.

Einsele, W. 1938. Über chemische und kolloidchemische Vorgänge in Eisen-Phosphat-Systemen unter limnochemischen und limnogeologischen Gesichtspunkten. Arch. Hydrobiol. 33: 361-387.

Fleischer, S. 1986. Aerobic uptake of Fe(III)-precipitated phosphorus by microorganisms. Arch. Hydrobiol. 107: 269-277.

Frevert, T. 1979. The pe redox concept in natural sediment-water systems; its role in controlling phosphorus release from lake sediments. Arch. Hydrobiol. Suppl. 55: 278-297.

Helbig J., H. Reissig and R. Holzig. 1981. Bestimmung von Nährstoff und Metallfreisetzungsraten aus Sedimenten umweltbelasteter Fliessgewässerstauhaltungen mit Hilfe von Inkubationsversuchen. Teil 1: Bestimmung von Phosphor und Eisenfreisetzungsraten. Acta Hydrochim. Hydobiol. 9: 203-212.

Gächter, R., J.S. Meyer and A. Mares. 1988. Contribution of bacteria to release and fixation of phosphorus in lake sediments. Limnol. Oceanogr. 33: 1542-1558.

Manning, P.G. and W. Jones. 1982. The binding capacity of ferric hydroxides for non-apatite inorganic phosphorus in sediments of the depositional basins of Lakes Erie and Ontario. Can. Minerol. 20: 169-176.

Manning, P.G., J.D.H. Williams, M.N. Charlton, L.A. Ash and T. Birchall. 1979. Mössbauer spectral studies of the diagenesis of iron in a sulphide-rich sediment core. Nature 280: 134-155.

Menzel D.W. and N. Corwin. 1965. The measurement of total phosphorus in seawater based on the liberation of organically bound fractions by persulfate oxidation. Limnol. Oceanogr. 10: 280-282.

Mortimer, C.H. 1941. The exchange of dissolved substances between mud and water in lakes. J. Ecol. 29: 280-329.

Nembrini, G. P., J.A. Capobianco, M. Viel and A.F. Williams. 1983. A Mössbauer and chemical study of the formation of vivianite in sediments of Lago Maggiore (Italy). Geochim. Cosmochim. Acta 47: 1459-1464.

Nürnberg, G.K. 1984. Iron and hydrogen sulfide interference in the analysis of SRP in anoxic waters. Wat. Res. 20: 369-377.

Nürnberg, G.K. 1987. A comparison of internal phosphorus loads in lakes with anoxic hypolimnia: laboratory incubations versus hypolimnetic phosphorus accumulation. Limnol. Oceanogr. 32: 1160-1164.

Nürnberg, G.K. 1988. The prediction of phosphorus release rates from total and reductant-soluble phosphorus in anoxic lake sediments. Can. J. Fish. Aquat. Sci. 45: 453-462.

Nürnberg, G.K., M. Shaw, P.J. Dillon and D.J. McQueen. 1986. Internal phosphorus load in an oligotrophic Precambrian Shield lake with an anoxic hypolimnion. Can. J. Fish. Aquat. Sci. 43: 574-580.

Psenner, R., R. Pucsko and M. Sager. 1984. Fractionation of organic and inorganic phosphorus compounds in lake sediments. Arch. Hydrobiol. Suppl. 70: 111-155.

Stainton M.P., M.J. Capel and F.A.J. Armstrong. 1977. The chemical analysis of freshwater. Can. Fish. Mar. Serv. Misc. Spec. Publ. 25: 180 p.

Stone, A.J. 1967. Least-squares fitting of Mössbauer spectra. J. Chem. Soc. A1967: 1966-1971.

Stumm, W. and J.J. Morgan. 1981. Aquatic Chemistry. Wiley, New York, 780 p.

Tessenov, U. 1974. Lösungs, Diffusions und Sorptionsprozesse in der Oberschicht von Seesedimenten, IV. Arch. Hydrobiol. Suppl. 47: 1-79.

Williams, J.D.H., JM. Jaquet and R.L. Thomas. 1976. Forms of phosphorus in the surficial sediments of Lake Erie. J. Fish. Res. Board Can. 33: 413-429.

Table 1. Average initial concentrations and changes in the sediment (ug g wet weight^{-1}) for 0-5cm (first row) and 5-10cm (second row) of matched cores. Changes in % of initial concentrations in last column. H_2O, water content (%), LOI, loss on ignition (%).

Compounds	Initial		Changes		%
	x	n	x	n	x
TP	306.8	3	-78.4	6	-26**
	381.8	2	-79.0	4	-21
TFe	3,234.8	3	-1037.3	6	-32***
	3,816.3	2	-1048.2	4	-27*
Mn	27.2	3	-3.4	6	-13
	41.0	2	1.2	4	3
BD-P	145.8	3	-31.3	6	-21***
	188.1	2	-74.3	4	-12
NaOH-P	55.6	3	12.9	6	23
	78.5	2	-12.7	4	-16
NAIP	283.0	2	-88.8	4	-31**
	171.5	2	-14.6	3	-9*
Apatite	10.9	2	-1.3	4	-12
	14.0	2	-1.5	3	-11
NaOH-Fe	218.0	3	37.2	6	17*
	184.7	2	35.7	4	19
Fe_{red}	897.9	2	-251.8	4	-28**
	976.2	2	-263.5	4	-27**
Fe_{ox}	2632.5	2	-768.8	4	-29**
	2661.2	2	-731.9	4	-28*
FeS_2	136.8	2	-32.0	4	-23
	180.7	2	-54.0	4	-30
H_2O	91.9	3	1.3	6	1*
	90.2	2	1.1	4	1*
LOI	27.6	3	1.3	6	5*
	25.6	2	2.7	4	11**

* $p < 0.05$
** $p < 0.01$
*** $p < 0.001$

Table 2. Height of sediment in small core, EH, pH and release rates (mg m^{-2} day^{-1}) after 26 or 27 (*) days of anoxic incubation, n = 12. Letters of cores refer to original (large) core, i.e., same letters mean the sediments stem from the same large core.

Core	Height (cm)	EH (mvolt)	pH	Release Rates TP	SRP	TRP	TFe	Fe2+	Mn
A1	5.0	244	na	0.26	0.10	0.65	18.65	2.13	4.35
A2	4.8	176	na	0.90	0.99	1.27	25.58	43.87	4.45
B2	4.2	204	na	2.79	2.81	3.07	47.15	56.64	3.93
B3*	4.7	81	6.57	4.09	4.31	4.42	50.71	61.25	3.64
C2*	7.0	108	6.71	8.54	3.01	5.73	99.40	91.57	3.45
E3	8.7	112	na	7.46	7.94	8.24	86.11	98.88	3.85
D2	10.0	115	na	7.01	8.09	8.11	78.25	98.80	2.93
D3*	9.7	63	6.52	7.09	7.52	6.83	75.94	103.07	2.99
E2	10.0	154	na	3.47	6.16	6.65	98.04	86.59	4.22
C3*	12.5	117	6.65	2.43	-0.26	2.92	38.11	48.97	2.65
F1*	14.5	107	6.81	5.21	4.48	5.26	72.19	83.68	3.65
F2*	15.0	93	6.80	6.03	3.56	5.61	66.05	81.89	3.53

na, data not available.

Table 3. Correlations of changes in sediment and water mass for matched cores (n=6, Pearson correlation coefficient).

Water	Sediment TP	Sediment TFe
TP	-0.84*	-0.85*
SRP	-0.94**	-0.96**
TRP	-0.92**	-0.94**
TFe	-0.79*	-0.73*
$Fe^{2}+$	-0.97**	-0.96**
Mn	0.47	0.64

* $p<0.05$
** $p<0.01$

Table 4. Molar TFe-to-TP ratios in the small cores before and after incubation and for the changes in matched cores, of the water and sediment (first row, 0-5 cm, second row, 5-10cm). Averages, SE in parentheses and n, number of cores.

	Before	After	Changes
Water	7.4 (2.6) 3	7.4 (0.6) 12	8.4 (1.5) 6
Sediment	6.3 (0.7) 3	5.8 (0.5) 12	8.4 (1.1) 6
	5.8 (1.0) 2	.5 (0.6) 8	10.6 (3.5) 4

FIGURES

Fig. 1. Typical water profile from Gravenhurst Bay of Oct. 1985 at a location close to the coring site. A. TP (square), SRP (open circle), total reactive P (closed circle) and EH (triangle). B. TFe (triangle), soluble Fe (open circle), free ferrous Fe (closed circle), Mn (square). C. Oxygen (open circle), sulfate (closed circle) and pH (square).

Fig. 2. Room temperature Mossbauer spectrum of the surface sediment (0-1 cm) of a representative core of Gravenhurst Bay. Inclusion of the pyrite doublet (FeS_2) slightly improved the fit of reduced and oxidized iron (chi-squared= 509, degrees of freedom= 491).

Fig. 3. Sediment profiles of a representative core of Gravenhurst Bay. A. TP (squares), BD-P (closed circles) NaOH-P (open circles) and TMn (triangles). B. TFe (closed squares), Fe_{ox} (closed circles), Fe_{red} (open square) and pyrite (open circles). C. Molar Fe-to-P ratios: total (closed square), NaOH extracted (open square) and Fe_{ox}-to-BD-P (triangle).

Fig. 4a. Changes in water and sediment mass of P (4a) and Fe(4b) for matched cores
Fig. 4b. (SE in parantheses, n=6), the regression lines are indicated for:
SRP= 40.7 (23.5) - 0.019 (0.003) Sediment-TP, r^2=0.89
Fe= 825 (201) - 0.017 (0.002) Sediment-TFe, r^2=0.93.

Fig. 5. Changes of Fe^{2+} in the water overlying the sediment and depth of sediment for all cores.

Fig. 6. Changes of TP in the water and redox potential (EH) of the water after incubation for all cores. Note that the increases in the water are small at EH above 160 mV, which is the theoretical threshold for the reduction of iron hydroxides.

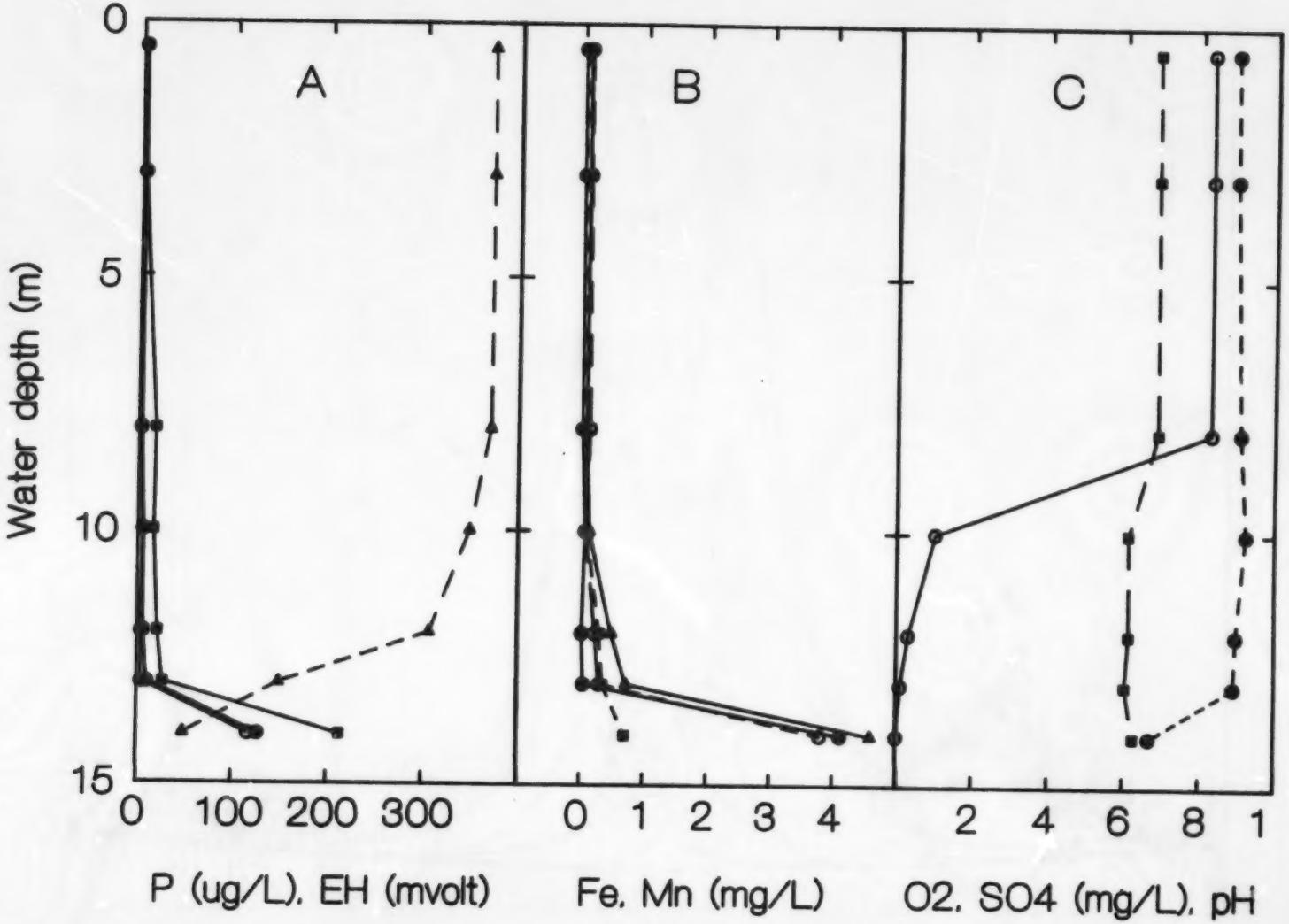
A
B
C
Water depth (m)
0
5
10
15
0 100 200 300
P (ug/L). EH (mvolt)
0 1 2 3 4
Fe. Mn (mg/L)
2 4 6 8 1
O2. SO4 (mg/L). pH

Figure 1

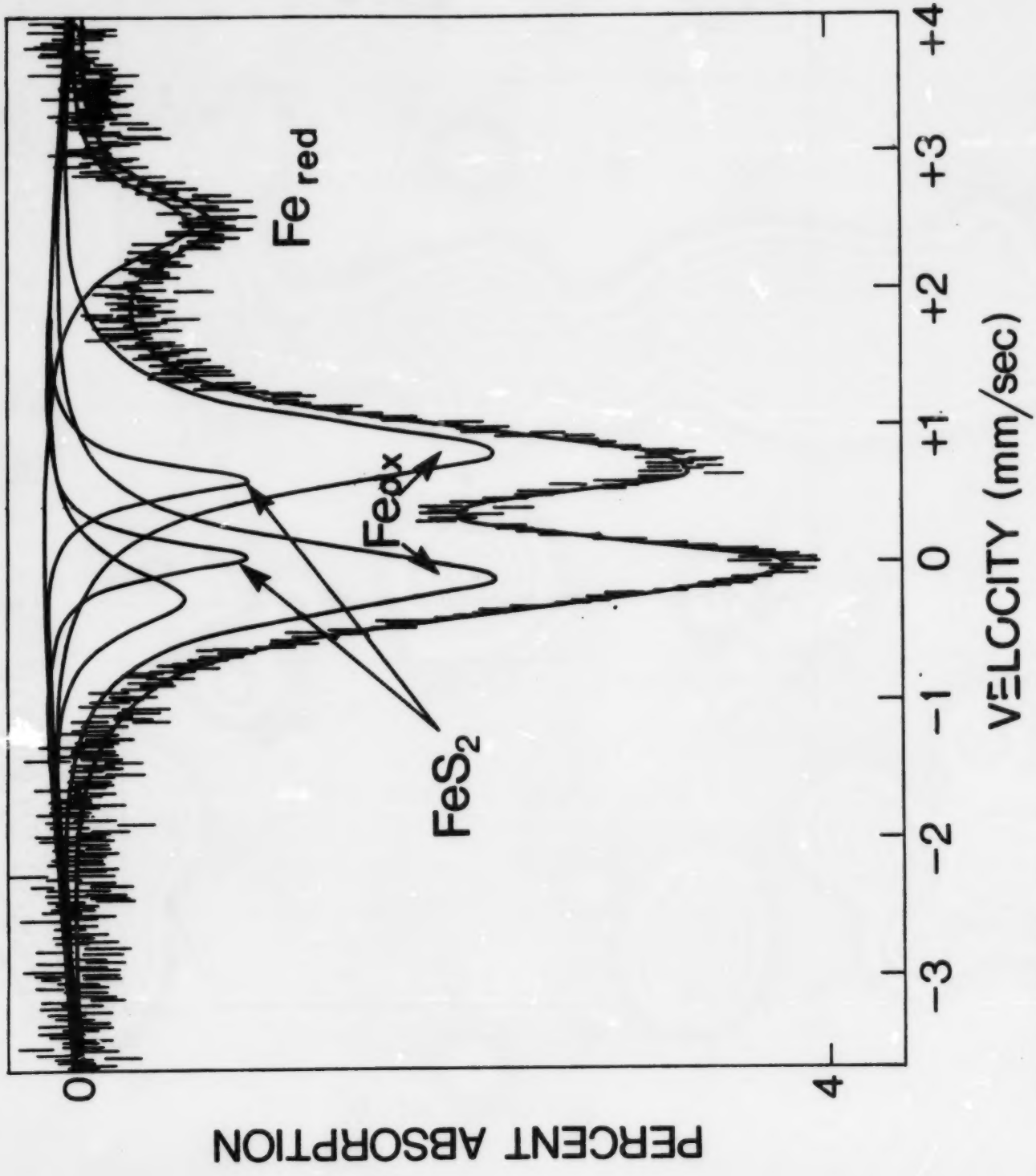
PERCENT ABSORPTION
0
4
−3
−2
−1
0
+1
+2
+3
+4
VELOCITY (mm/sec)
Fe red
Fe ox
FeS2

Figure 2

Sediment depth (cm)
0
5
10
A
B
C
0
1
2
P or Mn (mg/g dwt)
0
10
20
30
40
Fe (mg/g dwt)
0
5
10
Molar Fe-to-P ratios

Figure 3

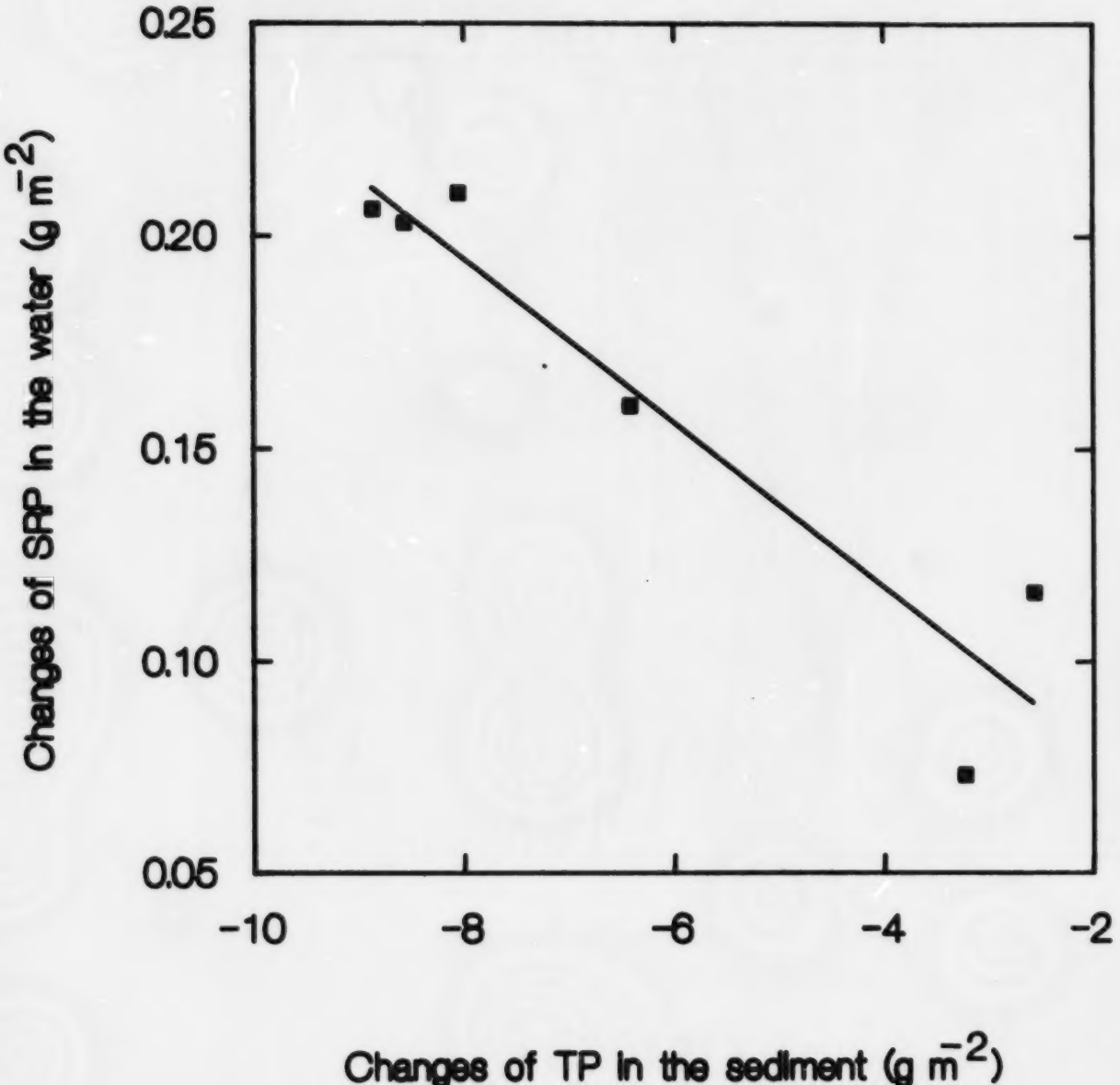
0.25
0.20
0.15
0.10
0.05
-10
-8
-6
-4
-2
Changes of SRP in the water (g m^{-2})
Changes of TP in the sediment (g m^{-2})

Figure 4a

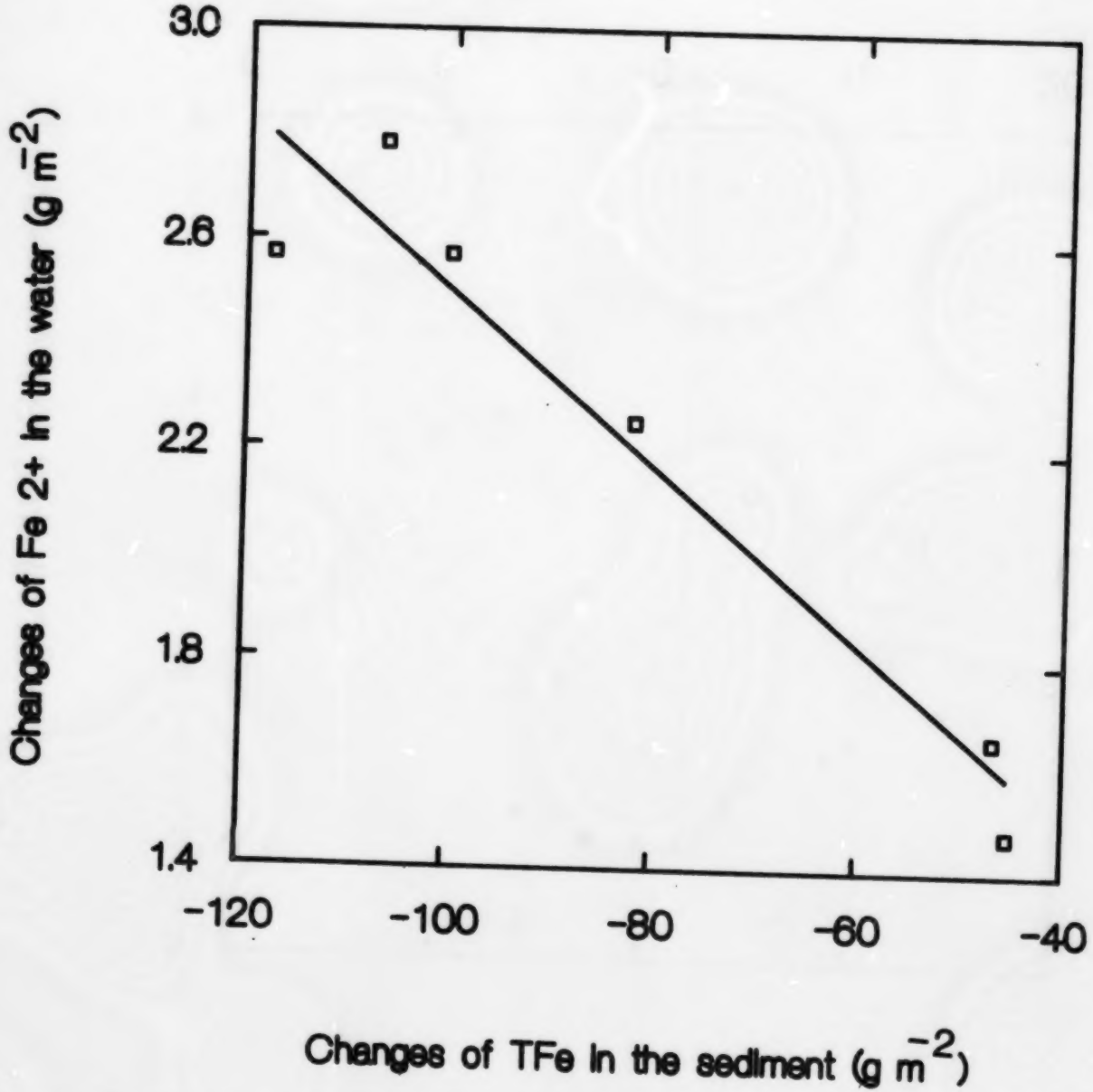
3.0
2.6
2.2
1.8
1.4
-120
-100
-80
-60
-40
Changes of Fe 2+ in the water (g m^{-2})
Changes of TFe in the sediment (g m^{-2})

Figure 4b

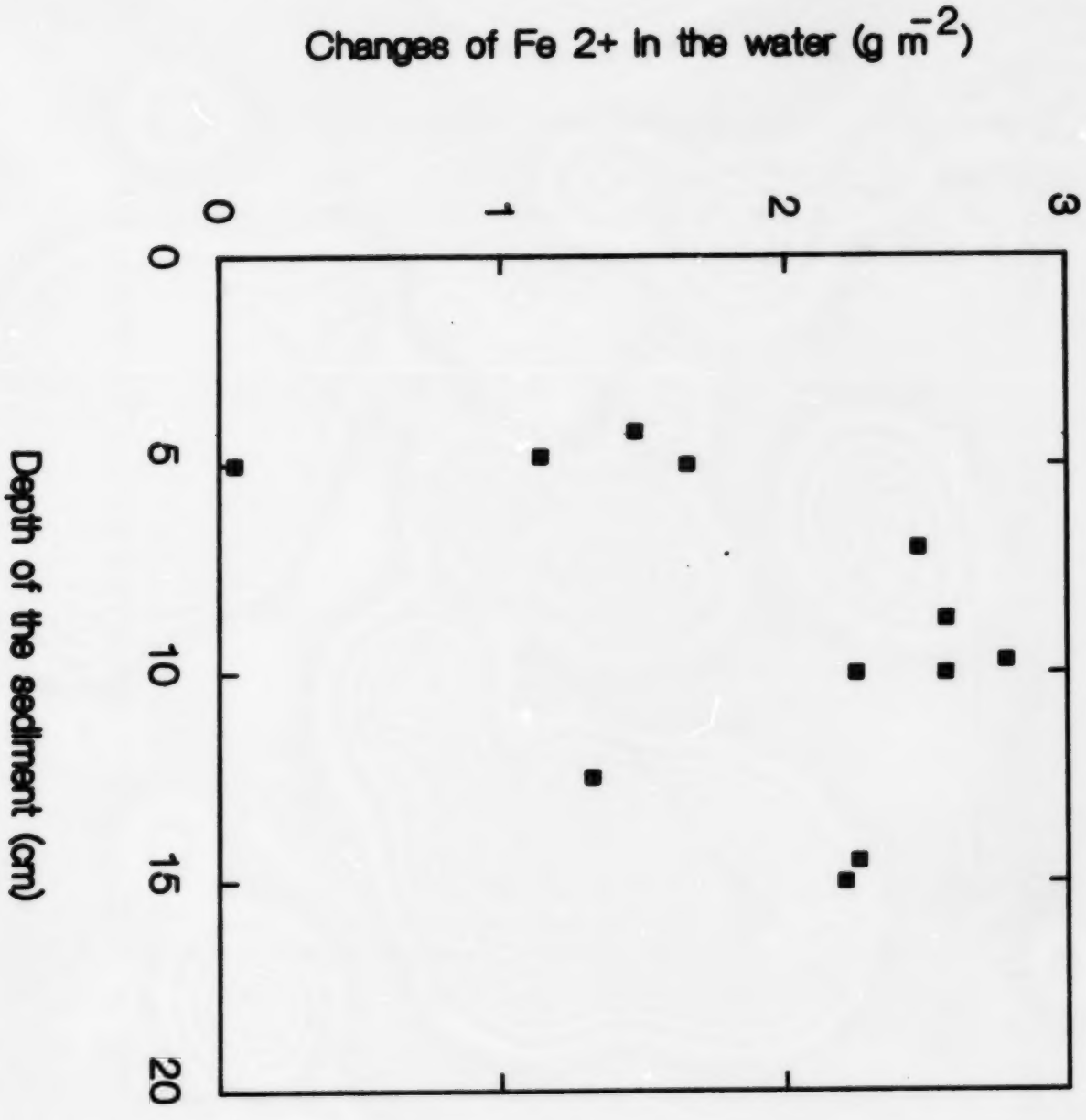
Changes of Fe 2+ in the water (g m^{-2})
0
1
2
3
0
5
10
15
20
Depth of the sediment (cm)

Figure 5

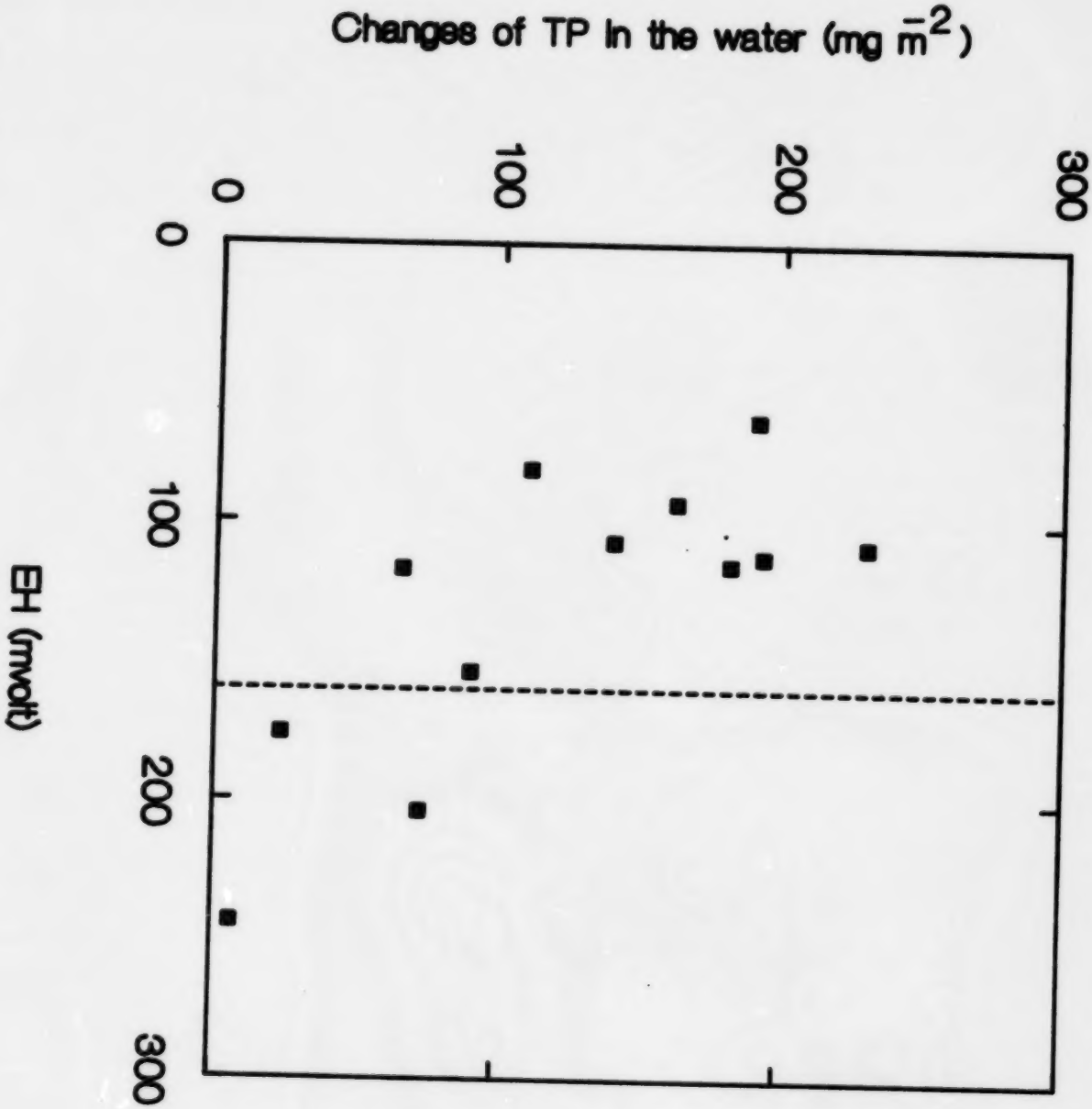
Changes of TP In the water (mg m^{-2})
0
100
200
300
EH (mvolt)
0
100
200
300

Figure 6